# REPORT DOCUMENTATION PAGE

*Form Approved OMB No. 0704-0188*



| 1. REPORT DATE *(DD-MM-YYYY)* | 2. REPORT TYPE | 3. DATES COVERED *(From - To)* |
|---|---|---|
| | Technical Paper | |

**4. TITLE AND SUBTITLE**

**5a. CONTRACT NUMBER**
F04611-93-C-0005

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**

**5d. PROJECT NUMBER**
3058

**5e. TASK NUMBER**
RF5C

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

ERC

**8. PERFORMING ORGANIZATION REPORT**

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

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AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

**10. SPONSOR/MONITOR'S ACRONYM(S)**

**11. SPONSOR/MONITOR'S NUMBER(S)**

**12. DISTRIBUTION / AVAILABILITY STATEMENT**

Approved for public release; distribution unlimited.

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**

**15. SUBJECT TERMS**

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | Leilani Richardson |
| Unclassified | Unclassified | Unclassified | (A) | | 19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015 |



1 item enclosed

122 036

TP-1998-068

30SPRFSC

93-C-0005

MEMORANDUM FOR PRS (Contractor Publication)

17 Mar 1998

FROM: PROI (TI) (STINFO)

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-1998-068**
K. Christe et al. "The New Bicyclic Nitrogen Tetroxide Cation, $NO_4^+$ has a Low Decomposition Energy"
**(Statement A)**

# THE NEW BICYCLIC NITROGEN TETROXIDE CATION, $NO_4^+$ HAS A LOW DECOMPOSITION ENERGY.*

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Nitrogen oxide cations, such as $NO_2^+$ and $NO^+$, are strong oxidizers and useful components for ionic High Energy Density Materials (HEDM) [1]. Their energy content and oxidizing power increase with increasing oxidation state of the nitrogen atom and the number of oxygen ligands. In our search for related, halogen-free, highly energetic cations we have become interested in the bicyclic $NO_4^+$ (I).

In view of the great challenge and the time consuming efforts which the synthesis of $NO_4^+$ would present, and the potential for low energy decomposition pathways, it was imperative to first pursue a feasibility study using *ab initio* methods. This contribution of theory offers the synthetic chemist the benefits of avoiding the unsuccessful pursuit of target molecules which are either vibrationally unstable or possess very low barriers towards decomposition, and provides guidance for their synthetic efforts.

The gas phase heat of formation of $NO_4^+$ (370 kcal/mol) has been estimated at the CCSD(T)/TZ2P level from the experimentally known heat of formation of $NO_2^+$ (233 kcal/mol) and the heat of the reaction:

$$NO_4^+ \rightarrow NO_2^+ + O_2\,(^3\Sigma_g^-) \quad \Delta E = 137 \text{ kcal/mol} \qquad (1)$$

Although the minimum $D_{2d}$ structure of **I** has short NO distances and long OO distances and is vibrationally stable at the HF, MBPT(2) and CCSD levels of theory (see Table 1), the decomposition barrier was suspected to be low because of the high exothermicity of reaction 1 (Scheme 1). The minimum energy $C_{2v}$ path is a symmetry and spin (singlet-triplet) forbidden reaction. To model the transition barrier structure we searched for its TS and the minima at the lowest PES crossings by using the novel STEOM-CCSD method. An algorithm, which allows to locate intersystem crossing

minima efficiently, has been implemented into the ACES II program recently. It is based on minimization of the functional, $F = E_1 + E_2 + \alpha * (E_1 - E_2)$, where $\alpha$ is an adjustable penalty parameter (usually about $10^3$).

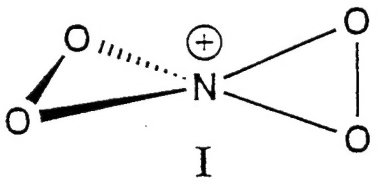
The transition state, which has been found at the $^1A_1$ potential energy surface, and two intersystem crossing minima, singlet-singlet and singlet-triplet, have similar structures and close energies (see Table 2). The wave function has an essential multi-configurational character in the transition state and in other computed low lying excited states (Scheme 2).

The estimated decomposition barrier has been finally computed by using CASPT2, STEOM-CCSD [2], and CCSD(T) methods with extended basis sets at the STEOM-CCSD/DZP optimized geometries. All approaches show the decomposition barrier to be too low (10-20 kcal/mol) for this cation to have any reasonable stability. In addition $NO_4^+$ has a high vertical electron affinity (8.4 eV compared to 4.5 eV in $NH_4^+$), which would be another reason for a high instability of the cation.

The structures of other bicyclic species, $XY_4$ (X = $B^-$, C, $N^+$; Y = N, O) (Scheme 3), have been computed at the MBPT(2)/6-31G* and at the CCSD/DZP levels (Scheme 3) and their energetics and reactivity are under investigation.


[1] E.W. Lawless, I.C. Smith, Inorganic High-Energy Oxidzers (Marcel Dekker, Inc. New York, 1968).

[2] M. Nooijen, R.J. Bartlett, J. Chem. Phys. 106 (1997) 6441.




I

$NO_2^+ + O_2$

?

137 kcal/mol

$NO_2\ (^2A_1) + O_2^+\ (^2\Pi_g)$

54 kcal/mol

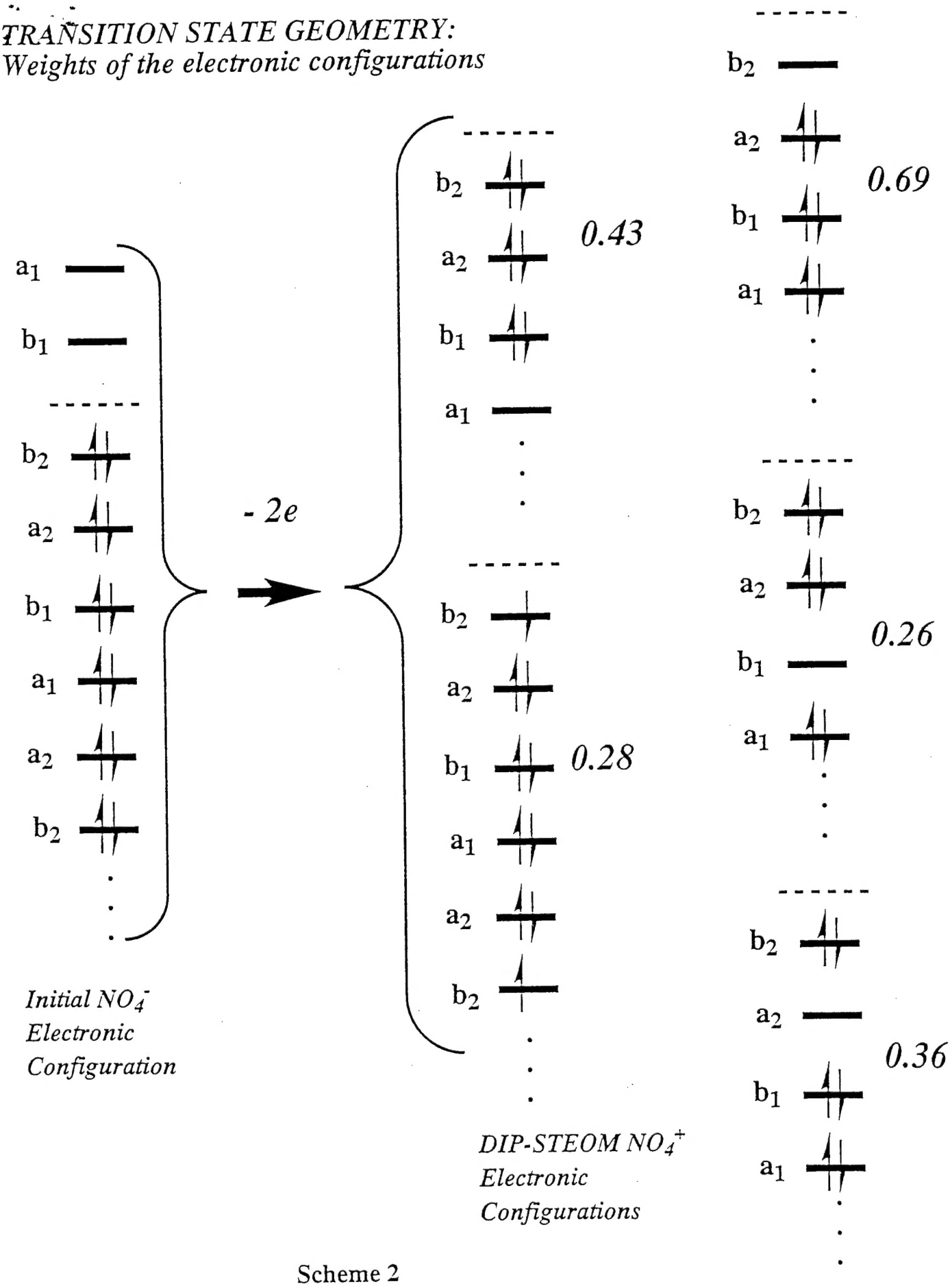
$NO_2^+ + O_2\ (^1\Delta_g)$

23 kcal/mol

$NO_2^+ + O_2\ (^3\Sigma^-_g)$

Scheme 1

*TRANSITION STATE GEOMETRY:*
*Weights of the electronic configurations*




*Initial $NO_4^-$ Electronic Configuration*

*DIP-STEOM $NO_4^+$ Electronic Configurations*

Scheme 2

# $XN_4$ vs $XO_4$

MBPT(2)/6-31G*
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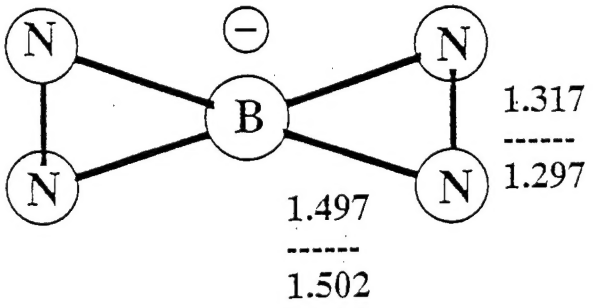
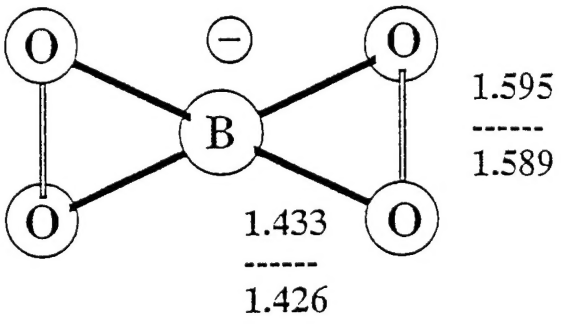
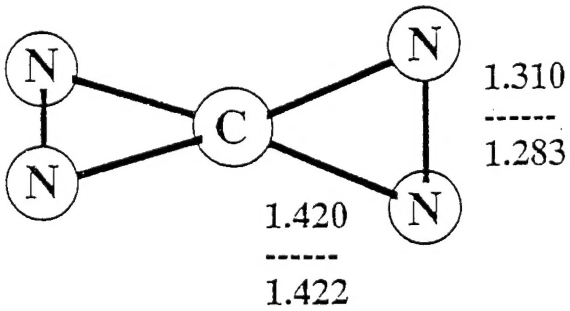
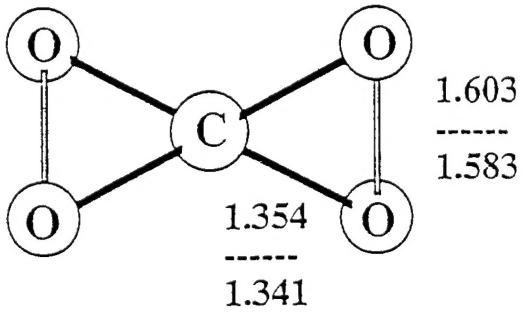
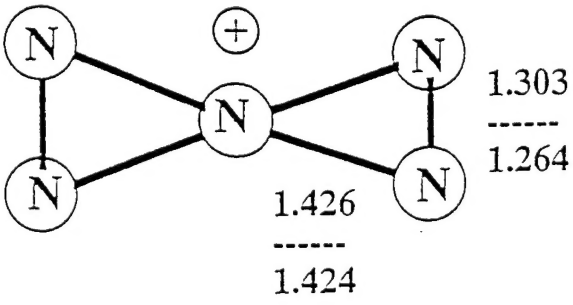
CCSD/DZP

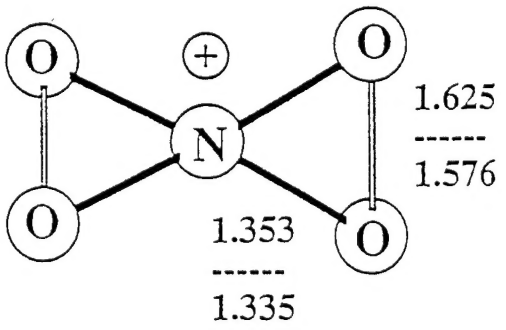



Scheme 3

Table 1.

Bond lengths (in angstroms) and harmonic vibrational frequencies (in $cm^{-1}$) of the $D_{2d}$ $NO_4^{+}$ [a]

| Method: | HF/ | | MBPT(2)/ | | CCSD/ | |
|---|---|---|---|---|---|---|
| | /DZP | /TZ2P | /DZP | /TZ2P | /DZP | /TZ2P |
| **Bond lengths:** | | | | | | |
| $R_{NO}$ | 1.290 | 1.292 | 1.346 | 1.347 | 1.335 | 1.335 |
| $R_{OO}$ | 1.455 | 1.467 | 1.620 | 1.613 | 1.576 | 1.571 |
| **Frequencies:** | | | | | | |
| $B_1$ | 472 (0) | 466 (0) | 341 (0) | 340 (0) | 376 (0) | 377 (0) |
| E | 556 (56) | 553 (46) | 511 (18) | 499 (16) | 505 (26) | 499 (24) |
| $A_1$ | 696 (0) | 689 (0) | 563 (0) | 571 (0) | 554 (0) | 567 (0) |
| $B_2$ | 942 (1) | 942 (4) | 664 (14) | 692 (15) | 679 (10) | 716 (12) |
| E | 1212 (24) | 1173 (17) | 967 (10) | 949 (10) | 1024 (16) | 1005 (26) |
| $A_1$ | 1231 (0) | 1218 (0) | 913 (0) | 929 (0) | 981 (0) | 998 (0) |
| $B_2$ | 1882 (100) | 1832 (100) | 1350 (100) | 1355 (100) | 1514 (100) | 1502 (100) |
| **Zero Point Energies:** | | | | | | |
| | 12.52 | 12.29 | 9.70 | 9.70 | 10.24 | 10.25 |

[a] Relative intensities are given in parenthesis.

Table 2.

Relative energies (in kcal/mol) and structures (bond lengths in angström) of the transition state and minima at the PES crossings for a $C_{2v}$ decomposition pathway at the STEOM-CCSD/PBS//CCSD-STEOM/DZP level.[a]

| MO confuguration | Energy | $R_{NO}^1$ | $R_{NO}^2$ | $R_{OO}^1$ | $R_{OO}^2$ |
|---|---|---|---|---|---|
| $D_{2d}$ $NO_4^+$ minimum | 0.0 | 1.335 | | 1.576 | |
| Transition State | 12.7 | 1.345 | 1.353 | 2.210 | 1.534 |
| $^1A_1$ - $^1B_1$ crossing | 12.6 | 1.343 | 1.353 | 2.196 | 1.532 |
| $^1A_1$ - $^3B_1$ crossing | 11.3 | 1.336 | 1.338 | 2.028 | 1.557 |

Lowest electronic state at the transition state geometry.

| Multiplet | root | irrep | energy diff (eV) | % singles | total energy |
|---|---|---|---|---|---|
| Triplet | 1 | $^3B_1$ | 14.52026902 | 99.98 | -354.00019085 |
| Singlet | 1 | $^1B_1$ | 14.72766231 | 99.96 | -353.99256929 |
| Singlet | 1 | $^1A_1$ | 14.73537610 | 99.86 | -353.99228581 |
| Singlet | 1 | $^1A_2$ | 14.78197499 | 99.94 | -353.99057334 |
| Singlet | 2 | $^1A_1$ | 14.83184913 | 99.87 | -353.98874050 |

[a] The $D_{2d}$ minimum has been computed at the CCSD/DZP level.